# HIGHLY INSULATING MONOCRYSTALLINE GALLIUM NITRIDE THIN FILMS

This application is a continuation of application Ser. No. 08/113,964, filed Aug. 30, 1993, now U.S. Pat. No. 5,538, 862, entitled "A METHOD FOR THE PREPARATION AND DOPING OF HIGHLY INSULATING MONOCRYSTALLINE GALLIUM NITRIDE THIN FILMS", which is a continuation of application Ser. No. 07/670,692, filed Mar. 18, 1991, which is abandoned.

## BACKGROUND OF THE INVENTION

This invention relates to a method of preparing monocrystalline gallium nitride thin films by electron cyclotron resonance microwave plasma assisted molecular beam epitaxy (ECR-assisted MBE). The invention further relates to a method for the preparation of n-type or p-type gallium nitride (GaN) films.

Efforts have been made to prepare monocrystalline GaN because of its potentially useful electrical and optical properties. GaN is a potential source of inexpensive and compact solid-state blue lasers. The band gap for GaN is approximately 3.4 eV, which means that it can emit light on the edge of the UV-visible region. For intrinsic GaN, the carrier concentration, $n_i$, is $5.2\times10^3$ $cm^{-3}$, the mobility is 330 $cm^2V^{-1}s^{-1}$ and the resistivity is $3.6\times10^{12}$ $\Omega$-cm.

Despite the desirability of a monocrystalline GaN film, its development has been hampered by the many problems encountered during the growth process. Previous attempts to prepare monocrystalline GaN firms have resulted in n-type films with high carrier concentration. The n-type characteristic is attributed to nitrogen vacancies in the crystal structure which are incorporated into the lattice during growth of the film. Hence, the film is unintentionally doped with nitrogen vacancies during growth. Nitrogen vacancies affect the electrical and optical properties of the film.

ECR-assisted metalorganic vapor phase epitaxy gave GaN films that were highly conductive and unintentionally doped n-type (S. Zembutsu and T. Sasaki *J. Cryst. Growth* 77, 25–26 (1986)). Carrier concentrations and mobilities were in the range of $1\times10^{19}$ $cm^{-3}$ and 50–100 $cm^2V^{-1}s^{-1}$, respectively. Efforts to dope the film p-type were not successful. The carrier concentration was reduced by compensation, that is, the effect of a donor impurity is "neutralized" by the addition of an acceptor impurity.

Highly resistive films were prepared by sputtering using an ultra-pure gallium target in a nitrogen atmosphere. The films were characterized n-type and the high resistivity was attributed to the polycrystalline nature of the films (E. Lakshmi, et al. *Thin Solid Films* 74, 77 (1977)).

In reactive ion molecular beam epitaxy, gallium was supplied from a standard effusion cell and nitrogen was supplied by way of an ionized beam. Monocrystalline films were characterized n-type, but higher resistivities of $10^6$ $\Omega$-cm and relatively low carrier concentrations and mobilities ($10^{14}$ $cm^{-3}$ and 1–10 $cm^2V^{-1}s^{-1}$, respectively) were obtained (R. C. Powell, et al. in "*Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors*" Vol. 162, edited by J. T. Glass, R. Messier and N. Fujimori (Material Research Society, Pittsburgh, 1990) pp.525–530).

The only reported p-type GaN was a Mg-doped GaN treated after growth with low energy electron beam irradiation. P-type conduction was accomplished by compensation of n-type GaN (H. Areario et al. *Jap. J Appl. Phys.* 28(12), L2112–L2114 (1989)).

Current methods of preparing GaN do not permit control of nitrogen vacancies within the lattice. Thus it has not been possible to prepare intrinsic GaN. Additionally, it is desirable to control the doping process in GaN films, thereby enabling the production of p-n junctions. The present invention presents a method to prepare near-intrinsic monocrystalline GaN films and to selectively dope these films n- or p-type.

## SUMMARY OF THE INVENTION

The method according to this invention for preparing highly insulating near-intrinsic monocrystalline GaN films uses ECR-assisted MBE. In a preferred embodiment, a molecular beam source of Ga and an activated nitrogen source is provided within an MBE growth chamber. The desired substrate is exposed to Ga and activated nitrogen. A film is epitaxially grown in a two step process comprising a low temperature nucleation step and a high temperature growth step. The nucleation step preferably occurs by exposure of the substrate to gallium and a nitrogen plasma at a temperature in the range of 100°–400° C. and the high temperature growth step is preferably carried out in the temperature range of 600°–900° C. Preferred substrates include, but are not limited to, (100) and (111) silicon and (0001), (11–20) and (1–102) sapphire, (111) and (100) gallium arsenide, magnesium oxide, zinc oxide and silicon carbide. The preferred source of activated nitrogen species is a nitrogen plasma which can be generated by electron cyclotron resonance microwave plasma or a hot tungsten filament or other conventional methods.

In a preferred embodiment, the nitrogen plasma pressure and Ga flux pressure are controlled, thus preventing the bearing of metallic gallium on the film surface and the forming of nitrogen vacancies within the lattice. The Ga flux is preferably in the range of $2.0–5.0\times10^{-7}$ torr. There is preferably an overpressure of nitrogen in the growth chamber, more preferably in the range of $10^{-3}–10^{-5}$ torr.

In yet another preferred embodiment, the low temperature nucleation step includes exposure of the substrate to Ga and nitrogen for a period of time in the range of 3–15 minutes. A film with a thickness of 200–500 Å is deposited, which is amorphous at the low temperatures of the nucleation step. The amorphous film can be crystallized by heating at 600°–900° C. in the presence of activated nitrogen. Subsequent treatment at higher temperatures, preferably 600°–900° C., results in the epitaxial growth of monocrystalline near-intrinsic GaN film. Preferred thickness of the growth layer is in the range of 0.5–10 μm.

In another aspect of this invention, the monocrystalline GaN film is preferentially doped n- or p-type. To generate a p-type semiconductor, the MBE growth chamber is equipped with Ga, activated nitrogen and acceptor sources. Acceptor sources include Group II elements such as Be, Zn, Cd, and Ca. The substrate is bombarded with electrons either by applying a positive bias to the substrate surface or a metal grid placed directly in front of the substrate. Conditions for low and high temperature deposition are as described above. Exposing the substrate to Ga, nitrogen and acceptor sources results in a doped GaN film, whereby the acceptor takes on an electron and is incorporated into the lattice as a negatively charged species. A charged acceptor species requires less energy to incorporate into the GaN lattice than a neutral acceptor. To dope the material n-type the substrate is bombarded with positive ions by biasing either the substrate or the grid negatively. Thus, the donor impurities incorporate into the GaN in their charged state. This requires less energy than to incorporate a neutral donor species. Suitable donors include Groups IV and VI elements.